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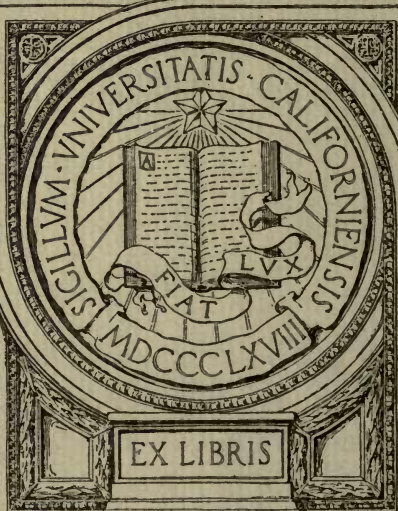
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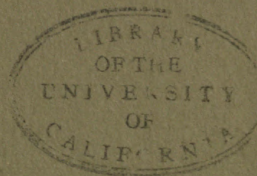
BY

PHILO F. HAMMOND

A THESIS

PRESENTED TO THE DEPARTMENT OF PHYSICS AND THE COMMITTEE
ON GRADUATE STUDY OF THE LELAND STANFORD JUNIOR
UNIVERSITY IN PARTIAL FULFILMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
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THE INFLUENCE OF THE METALLIC IONS IN AN ELECTROLYTIC SOLUTION UPON THE ELECTRIC POTENTIAL OF A METAL PLACED IN THE SOLUTION.

It is well known that a metal when placed in water or in an electrolytic solution may become more electropositive or electronegative than it was before being placed in the water or the solution. When the metal becomes electronegative in the water or solution it is presumably because some of its electropositive ions have escaped into the solution. When the metal becomes electropositive, it is supposed to be because ions of hydrogen or some other ions more electropositive than the metal have been deposited upon it.

Since in order that the electropositive ions may escape from the surface of a metal or the electropositive and electronegative ions of a compound may dissociate it becomes necessary that the force of cohesion or of affinity must be lessened, and since it seems to be definitely established that both cohesion and affinity are manifestations of the attraction between oppositely electrified ions, it has come to be believed that the weakening of these forces in water and other solvents is due to the high specific inductive capacity of the solvent.

From this point of view, a metal should more readily dissolve in a solvent of high specific inductive capacity than in one of low specific inductive capacity, and it should also become more electronegative in the former than in the latter.

It has been maintained by Professor Sanford that the metals, themselves, have specific inductive capacity, and that the more electropositive a metal the higher its specific inductive capacity.* This being the case, if two equimolecular solutions of salts having the same acid ion but different metallic ions be prepared, the solution containing the more electropositive metallic ions should have a higher specific inductive capacity than the solution having the more electronegative metallic ions, and the same piece of metal placed alternately in one solution and in the other should become more electronegative in the solution containing the more electropositive metallic ions than in the other solution.

Professor Sanford tested this hypothesis with equimolecular solutions

* See "Specific Inductive Capacity and Atomic Charges," *Phys. Rev.*, N.S., I, 446, and "The Specific Inductive Capacity of Certain Metals," *Ibid.*, VIII, 89.

of zinc sulphate and copper sulphate, using four different metals as electrodes, and he found that in every case the electrode in the zinc sulphate solution became more electronegative than an electrode of the same metal in the copper sulphate solution.

Miss Florella K. Finney* then tried the same experiment with a large number of salts in equimolecular water solutions, using several different metals as electrodes, and found that in every case when two electrodes of the same metal are immersed in communicating equimolecular solutions of the corresponding salts of different metals, the electrode in the solution containing the more electropositive metallic ion became the anode, and the electrode in the other solution became the cathode of an electrolytic cell. Miss Finney determined in this way the order of the apparent specific inductive capacities of the metallic ions as follows: Potassium, sodium, ammonium, barium, calcium, zinc, nickel, hydrogen, copper and ferric-iron.

Miss Finney made no attempt to measure the electromotive forces set up between two similar electrodes by the different metallic ions of the solutions in which they were immersed. The present paper gives the results of an attempt to determine the magnitude of these electromotive forces by the condenser method.

Five paper condensers were used, having a capacity of about two micro-farads each. These condensers were found to be very satisfactory for the purpose, the absorption being so small as to produce no appreciable error. No attempt was made to obtain the exact capacity of the condensers, but the throw of the ballistic galvanometer through which they were discharged was calibrated by means of a Siemens and Halske voltmeter reading to 0.02 volt. The value of one division of the galvanometer scale was determined for different parts of the scale and on both sides of the zero. This value varied but little for different parts of the scale, and was about 0.0028 volt for the larger deflections and about 0.00275 volt for the smaller deflections. The arrangement was capable of measuring an electromotive force accurately to ± 0.0001 volt, so far as galvanometer and condensers were concerned, but the variations in the electromotive forces being measured were much greater than this amount.

The condensers were charged from two electrodes of the same metal which were placed in vessels containing the two solutions which were being tested. For the purpose of establishing communication between the two solutions several different arrangements were tried, and four

* "The Influence of the Metallic Ion in Electrolytic Solutions Upon the Potential Differences Between the Solutions and a Metallic Electrode," *Phys. Rev.*, VI, 400 (1915).

different forms of cell were used with most of the solutions. In three of these forms the contact was made by means of a capillary extension from the bottom of one or both the vessels containing the solutions. One of these capillaries dipped into an expansion of the other, or both dipped into another vessel containing one of the solutions or merely distilled water. The whole purpose of the different arrangements was to make diffusion between the two solutions as small as possible, and to keep the solutions about the two electrodes pure. In one form of cell an ordinary U-tube had its bend filled with gelatine and the two solutions were placed one on each side of this plug. This was the arrangement which was used in most of Miss Finney's experiments. The deflections of the galvanometer were usually more consistent among themselves with this cell than with the others, and they usually agreed closely with those taken by means of the other cells. In only one or two cases were there differences which seemed greater than the experimental errors due to other causes.

The solutions used were nearly all one tenth normal, but a few of them, which had been prepared by Miss Finney, were one tenth molar. However, there was no noticeable difference between the results obtained with the two classes of solutions.

The salts tested were in most cases the nitrates, but in some case chlorides and sulphates were used. The metal electrode in the solution which was being tested was compared with a similar electrode of the same metal in a solution of silver nitrate and also in a solution of a potassium salt of the same acid ion as the salt under examination. The silver and potassium salts were chosen because their ions were as near the opposite ends of the voltaic series as any which were easily obtainable. Since the electrode in the solution under examination was always electro-positive to the electrode in the solution of potassium salt and electro-negative to the electrode in the silver nitrate solution, the sum of the electromotive forces determined with the two should equal the electromotive force between the same electrodes when one was in the solution of the potassium salt and the other was in the silver nitrate solution.

The results here given are taken from data obtained with platinum electrodes only. Many of them were repeated with the same general results with silver electrodes, but the variations between different sets of readings were greater with these than with the platinum electrodes.

Before making a set of readings the electrodes were carefully cleaned and were put into their respective electrolytes, which were brought into communication as short a time as possible before the condenser was charged. The condenser was then charged and discharged through the galvanometer, successive charges being used as rapidly as conditions

would permit. Usually from five to twenty galvanometer deflections were taken in this way for each of the four cells. The mean value of these was then taken as the most probable value. The electromotive force of the combination was then computed from the constants of the apparatus.

In several cases some one of the cells used did not give as consistent results as the others, and in a few cases the readings from one cell had to be thrown out.

In many cases it was difficult to know just how long to allow the condenser to charge, since it sometimes took longer to reach its maximum charge than the resistance and capacity of the circuit seemed to warrant. Sometimes, also, each successive charge was slightly smaller than its predecessor, while in other cases each charge was slightly larger than the preceding one. In either of these cases a careful cleaning of the electrodes usually brought the charge back to its original magnitude. On the other hand, the cleaning of the electrodes might introduce a small error by leaving one in a different condition from the other. This could be detected by putting both electrodes into a vessel of distilled water.

No satisfactory results could be obtained with some salts, as, for example, bismuth nitrate, which forms bismuth oxy-nitrate and nitric acid when put in water.

The errors were probably of nearly the same magnitude, regardless of the electromotive force of the combination, hence the per cent error is usually greatest for two solutions in which the electrodes gave a low electromotive force. Since each solution was tried against two others, one of which gave an electromotive force in the opposite direction from the other, if it was near one solution in its properties it was correspondingly distant from the other, and if the per cent error was large with the one it was correspondingly small with the other.

The greatest difference in voltage indicated by the different cells with the same solution was in a very few cases slightly greater than 0.025 volt, but this was very unusual. The indications of the different cells usually agreed to within a few thousandths of a volt. As examples, with barium nitrate and silver nitrate the electromotive forces indicated by the different cells were 0.622 volt, 0.624 volt, 0.622 volt and 0.633 volt. With cadmium nitrate and silver nitrate the same cells gave 0.588 volt, 0.599 volt, 0.610 volt and 0.585 volt.

Considerable difficulty was experienced with some combinations. This was especially true when nitric acid was used with either silver nitrate or potassium nitrate. This was perhaps due to the rapid diffusion of the hydrogen ion into the solution containing the metallic ion, since

in the case of the silver nitrate solution the electromotive force increased very rapidly, while in the case of the potassium nitrate solution it decreased very rapidly. In the case of this solution the cell containing the gelatine plug was the only one which could be used successfully, and this for only two or three trials before the cell had to be renewed. Ferrous sulphate was also a troublesome solution.

TABLE I.

Electromotive force between two platinum electrodes when one was in a solution of silver nitrate (Column II) or potassium nitrate (Column III) and the other was in a normal solution of the salt named in Column I.

I. Salt in the Solution Which Contained One Electrode While the Other Was in a Solution of Silver or Potassium Nitrate.	II. E.M.F. When One Electrode Was in a Solution of Silver Nitrate.	III. E.M.F. When One Electrode Was in a Solution of Potassium Nitrate.	IV. Sum of Electro- motive Forces in Columns II and III.	V. Variation From Mean.
AgNO ₃	0.000	0.650	0.650	+0.004
Fe(NO ₃) ₃	0.112	0.536	0.648	+0.006
Cu(NO ₃) ₂	0.397	0.269	0.666	-0.012
HNO ₃	0.509	0.149	0.658	-0.004
Pb(NO ₃) ₂	0.532	0.119	0.651	+0.003
Ni(NO ₃) ₂	0.560	0.090	0.650	+0.004
Co(NO ₃) ₂	0.570	0.093	0.663	-0.009
FeSO ₄	0.591	(0.067) (K ₂ SO ₄)	0.658	-0.004
Cd(NO ₃) ₂	0.594	0.063	0.657	-0.003
Zn(NO ₃) ₂	0.608	0.068	0.668	-0.014
MnCl ₂	0.614	0.047 (KCl)	0.661	-0.007
Al ₂ (SO ₄) ₃	0.619	(0.043) (K ₂ SO ₄)	0.662	-0.008
Mg(NO ₃) ₂	0.612	0.032	0.644	+0.010
Ca(NO ₃) ₂	0.622	0.028	0.650	+0.004
Ba(NO ₃) ₂	0.625	0.014	0.639	+0.015
KNO ₃	0.650	0.000	0.650	+0.004
KCl.....	0.649	0.000	0.649	+0.005
K ₂ SO ₄	0.652	0.000	0.652	+0.002
Mean.....			0.654	±0.007

On account of these difficulties, a high degree of accuracy in the determination of the electromotive forces is not claimed. In general, the figure in the third decimal place is too unreliable to have significance and these figures are given only to show the relative position of the ions of the various metals. The relative values given are probably accurate to ± 0.01 volt, and the absolute values to ± 0.02 volt.

In Table I are given the results obtained with the various solutions used with platinum electrodes. The values given in column III for

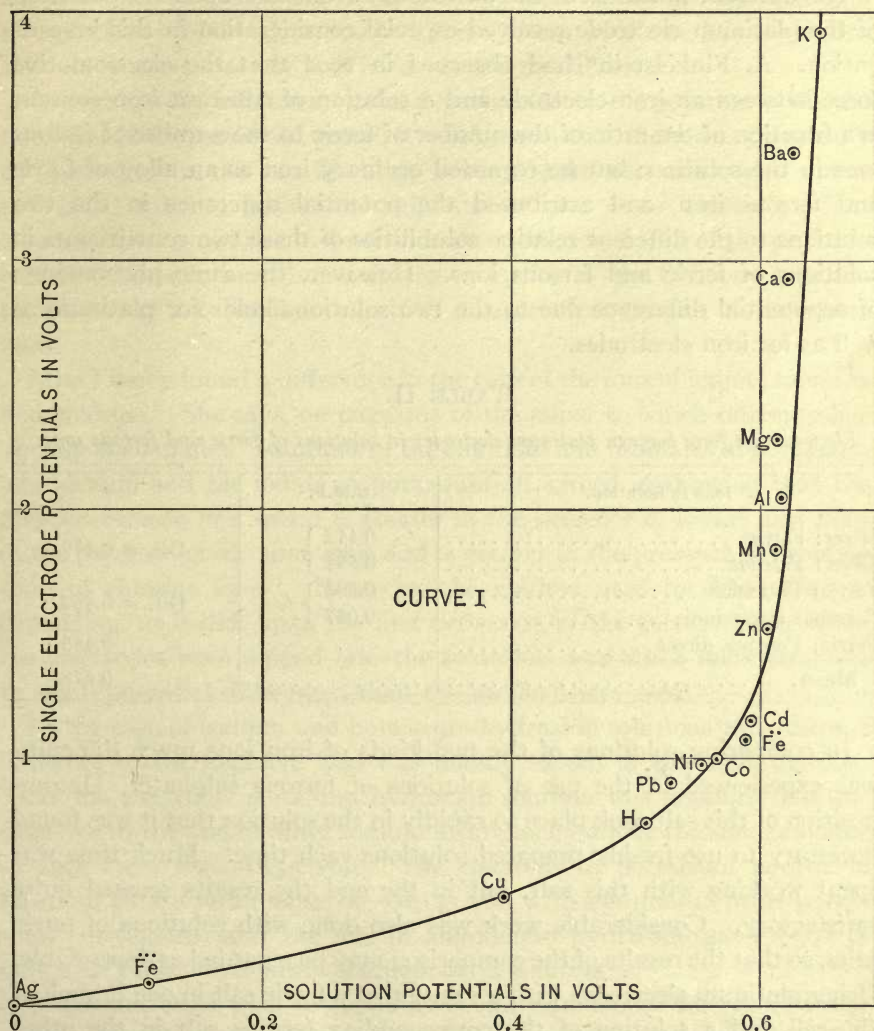
calcium and barium have been corrected. The electrodes were changed just before these results were obtained and the deflections were taken in one direction only. Afterwards it was found that the electrodes gave a considerable deflection in the same direction in distilled water. This was accurately determined and subtracted from the original deflections. Otherwise the quantities given are all as they were originally determined.

It will be observed, as was shown by Miss Finney, that the influence of the metallic ions in the solution was such as to make the platinum electrode in the solution containing the more electropositive ion the anode of the electrolytic cell, and hence that when the metals are arranged in the order of the electromotive force which their ions in solution give against a solution of silver ions, they are also arranged nearly in the order of the electromotive series as determined by chemical displacement, the exceptions being probably due to small experimental errors.

In the tables of single electrode potentials of the different metals in normal solutions of their own salts, we have quantities which differ from those here given in that in the present investigation the same metal is used with all the solutions, instead of each metal being used in a solution of its own ions. The difference in the quantities measured in the two cases, if the single electrode potential of silver in silver nitrate be taken as zero, is then the difference in the potential change induced by dipping a metal into a normal solution of a salt containing its own ions and the potential change induced in platinum by dipping it into the same solution.

In Curve I the two quantities above mentioned are plotted against each other, the quantities measured in this investigation being called the solution potentials and used as the abscissæ in plotting the curve. It will be seen that for the metals usually classed as electropositive the single electrode potential varies with a change of solution much faster than does the solution potential, while for the more electronegative metals the opposite is the case. It should be remembered in this connection that in the case of the single electrode potential both the metal electrode and the metallic ions of the solution are different in each case, while for the solution potential here discussed the same electrode is used in all the solutions. Then, too, the electropositive metals change their potential when put into a solution by giving off their positive ions to the solution, while the electronegative metals change their potential by taking up hydrogen or other positive ions from the solution. It follows that in the case of the single electrode potential of the electropositive metals the difference in the solubilities of the metals, them-

selves, is added to the differences produced by a change in the specific inductive capacity of the solution. The greater change in the single electrode potential than in the solution potential of these metals follows as a necessity from the Sanford hypothesis, since the cohesion of the metal, itself, depends upon its specific inductive capacity, and hence those metals whose ions give the higher specific inductive capacity to the solution are the ones whose own solubilities are, for the same reason, greater.



In case of the electronegative metals, since their potential change in solution is caused by the deposition upon them of positive ions from the solution, their own solubility can play no part. The differences in the

cohesion of the metal for the positive ions of the solution must accordingly play the whole part in the potential differences produced by the same solution upon different metals. Since platinum has a higher cohesion than any of the metals whose solutions were used in this investigation, it has a stronger attraction for the positive ions of all the solutions than any of the others; *i. e.*, it is more electronegative to all the solutions than any of the other metals.

The different influence of the ferric and ferrous ions upon the potential of the platinum electrode received especial consideration in this investigation. A. Finkelstein* had observed in 1902 that the electromotive force between an iron electrode and a solution of constant iron content is a function of the ratio of the number of ferric to the number of ferrous ions in the solution; but he regarded ordinary iron as an alloy of ferric and ferrous iron, and attributed the potential difference in the two solutions to the different relative solubilities of these two constituents in solutions of ferric and ferrous ions. However, the same phenomenon of a potential difference due to the two solutions holds for platinum as well as for iron electrodes.

TABLE II.

Electromotive force between platinum electrodes in solutions of ferric and ferrous ions.

Ions in Solution.	E.M.F.	
Silver: Ferric.....	0.112 }	Dif. = 0.479
Silver: Ferrous.....	0.591 }	
Ferric: Potassium.....	0.536 }	Dif. = 0.469
Ferrous: Potassium.....	0.067 }	
Ferric: Ferrous, direct.....		0.486
Mean.....		0.478

In comparing solutions of the two kinds of iron ions much difficulty was experienced in the use of solutions of ferrous sulphate. Decomposition of this salt took place so rapidly in the solution that it was found necessary to use freshly prepared solutions each time. Much time was spent working with this salt, but in the end the results seemed quite satisfactory. Considerable work was also done with solutions of ferric salts, so that the results of the comparison may be regarded as dependable. Using platinum electrodes with a solution of a ferric salt in one branch of the cell and a solution of the corresponding ferrous salt in the other branch the electromotive force between the two electrodes was found to be 0.486 volt. This value determined indirectly is shown in Table II.

* *Zeitsch. f. phys. Chem.*, XXXIX, 91.

It will be seen that the values determined for the ferrous ions correspond to the values of single potential difference usually given. If we use the mean value of the solution potential determined for ferric ions and determine its corresponding single electrode potential from the curve, we find it to be about -0.938 volt. This is in close agreement with the results of an unpublished research on the passive state of iron by Prof. J. G. Brown. Sanford* has shown that from the indications of all its properties depending upon cohesion iron should fall between gold and platinum in the electromotive series, from which he has concluded that the passive state of iron is its normal condition.

As regards the influence of the negative ion in the solution upon the potential of the immersed metal, it will be seen that there was practically no difference in the results when silver nitrate was used with either potassium nitrate, potassium sulphate or potassium chloride. Considerable work was done to determine the influence, if any, of the negative ions in other solutions, but with the exception of the OH ion these differences were too small to admit of measurement by the method here used.

Miss Finney found a difference in the case of the ions of iodine, bromine and chlorine. She says, on page 402 of the paper to which reference has already been made: "Solutions of the chlorides and bromides of potassium and sodium and the iodide of potassium all agreed in showing that the solution tension of a metal is greater in the presence of iodine ions than in the presence of bromine ions, and is greater in the presence of bromine than of chlorine ions." However, the method used by Miss Finney, depending, as it did, upon the first deflection of the galvanometer when the electrodes were dipped into the solutions, was much more sensitive to small potential differences than the method here used.

In the case of sodium and potassium hydroxide solutions the different influence of the negative ions was plainly shown in this investigation. Thus the electrode in sodium hydroxide solution was regularly electro-negative to the one in other sodium solutions by about the same amount in each case, viz., 0.135 volt. The electrode in potassium hydroxide solutions gave a mean value of -0.143 volt with solutions of other potassium compounds, and the one in ammonium hydroxide gave -0.031 volt with other ammonium compounds in solution.

In conclusion, I wish to thank Professor Sanford for his interest and advice throughout the work and for his assistance in the revision of this paper. I wish also to thank Mr. Bol for making the glass cells used.

* *Phys. Rev.*, XXVI, 410 (1908). "A Physical Theory of Electrification," Stanford University Publications, University Series, No. 6, 1911, p. 44.

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